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Review

# Synthesis of polymers from organic solvent liquefied biomass: A review

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ABSTRACT

Biomass liquefaction with organic solvents is a unique thermochemical conversion process for biomass utilizations. It combines the useful functional groups from both biomass and organic solvents used in liquefaction, thus obtaining a large variety of polymers. This review is focused on the resin products synthesized from organic solvent liquefied biomass, including phenolic, polyurethane, epoxy, polyesters, etc. Many biomass species, such as wood, corn stover, waste paper, and wood bark, have been investigated as the feedstocks for liquefied biomass-based resin products. Phenol liquefied biomass was studied the most mainly based on expectation to utilize the aromatic structures of lignin in biomass as the substitute for phenol in phenolic resin synthesis. Further condensation reaction of phenol liquefied biomass with formaldehyde to synthesize novolac or resol phenolic resins was proven to be an efficient route to convert the un-reacted phenol from liquefaction to resins and improve the physical mechanical properties of the resulting resins. Except for phenolic resins, most other polymers from liquefied biomass were synthesized based on the utilization of hydroxyl groups in liquefied biomass. Polyhydric alcohols liquefied biomass was used as polyols to synthesize polyurethanes, epoxy, and polyesters. To achieve comparable mechanical strength of resulting resin products, the common liquefaction solvent to biomass ratio was 3/1, which indicates a biomass substitution around 25% to petroleum raw materials. A few cases could reach 50% substitution with biomass pretreatment before liquefaction. Three main concerns with the liquefied biomass-based resins were their relatively higher viscosities, highly hydrophilic characters, and relatively lower cross-linking density in cured resins.

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**Contents**



## 1. Introduction

Polymers touch our lives as does no other class of materials from small candy wrapper to the artificial heart, with no end to new uses and improved products in sight [1]. The world plastics consumption has consistently grown for decades and was about 268 million tonnes in 2007 [2]. Production of polymers has long relied on fossil resources to provide raw materials. However, increasing concerns have been raised with this massive consumption of fossil oil. First of all, usage of fossil oil is considered a big contributor to increase the level of carbon dioxide ($CO_2$), the major part of greenhouse gas, which is directly associated with the global warming and climate change [3]. Disposal of polymer waste is another highly visible environmental problem because the synthetic polymers are highly resistant to natural degradation. In addition to the environmental issues, the ultimate problem with petroleum based materials

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is the ever declining proven fossil reserves and increasing demand in both developing and developed countries, which has caused the skyrocketing of the price of petroleum products. All these concerns have become the major drivers in finding alternative renewable resources for energy and chemicals.

Biomass is a promising resource that can replace fossil oil for sustainable production of bio-fuel and chemicals. It is the most abundant renewable resource on earth. With a yearly production of about $20 \times 10^{10}$ tonnes, only 3% is used in non-food areas, such as paper and pulp industries [4]. Biomass is far less expensive than other resources, such as crude oil and natural gas, for energy and chemical production based on energy content [4]. They are short growing cycle plants. Burning fuel or producing products from biomass do not add net $CO_2$ to the atmosphere. In other words, they are carbon neutral. Plant biomass is composed primarily of cellulose ($[C_6(H_2O)_5]_n$), hemicellulose ($[C_5(H_2O)_4]_n$), and lignin ($[C_{10}H_{12}O_3]_n$), as well as a small amount of pectin, protein, extractives and ash. They are also called lignocellulosic biomass. Hereafter, the biomass discussed in this review is lignocellulosic biomass. In a sense, the tissues of lignocellulosic biomass are comparable to fiber-reinforced composites in which the lignin represents the plastic binder and the cellulose the reinforcing fibers [5]. Typically, dry lignocellulosic biomass contains 40–45% cellulose, 25–35% hemicelluloses, 15–30% lignin and up to 10% other compounds. Cellulose is a polymer of D-glucose linked together by β-1,4-glucoside bonds with a degree of polymerization up to 10,000 or higher. Hemicellulose is an oligomer of both C6 and C5 sugars and has a degree of polymerization below 200. Agricultural residues and hardwood are rich in pentose sugar xylose, whereas softwood species are rich in hexose sugar mannose [6]. Lignin is a highly cross-linked, three-dimensional aromatic polymer consisted of phenylpropane units linked together by C–C or ether bonds. In view of their chemical compositions, all three of these wood components may serve as interesting basic materials for various polymers with high added values.

Efforts have been made for decades on utilization of biomass for bio-based products. In general, the main routes for biomass to bio-fuel and chemicals are based on biochemical and thermochemical conversions. Biochemical conversion breaks down biomass to sugars using either enzymatic or chemical process and then converts sugars to ethanol via fermentation. Products from this process are not within the scope of this review. Thermochemical conversions includes gasification, pyrolysis, and liquefaction. In gasification, lignocellulosic feedstocks are converted to synthetic gas, primarily CO and $H_2$, using heat at temperatures up to 1000 °C. Pyrolysis is the thermal degradation of biomass by heat in the absence of oxygen to obtain charcoal, bio-oil, and fuel gas. There are two types of liquefaction involved thermochemical processes. The first type, also called direct liquefaction, is similar to pyrolysis but conducted at lower temperature and normally under pressures of about 5–10 MPa [7]. The other liquefaction process dissolves biomass in organic solvents with or without a catalyst at moderate temperatures (100–250 °C). Research on the latter could be traced back to the 1980s and was first aimed to improve the flowability and reactivity of lignocellulosic biomass. To accomplish the goal, lignocellulosic biomass was decomposed to relatively low molecular weight substances via solvolysis with organic solvents. The resulting liquid products were used to prepare different polymeric materials depending on their specific reactive groups. Organic solvents that have been used for liquefaction include phenol, polyhydric alcohols, ethylene carbonate, etc. Different processing methods also have been studied, such as microwave-assistant liquefaction.

There have been several reviews on bio-based products from biomass pyrolysis [8–10]. Therefore, they are excluded from the present review. The focus of this review is on the resin products from organic solvent liquefied biomass. Different categories of resins were synthesized from liquefied biomass, including phenolic, polyurethane, epoxy, etc. Their synthesis methods and the applications to adhesives, film, and so on are also discussed.

## 2. Phenolic resins from liquefied biomass

Phenol has long been used in the organosolv pulping process in that lignin could be dissolved in phenol while cellulose was less attacked and had a quality suitable for paper production [11]. It is also one of the most popular solvents in biomass liquefaction in that lignin has a similar structure to phenolic resin. Based on this similarity, it is expected that phenol, the most costly raw material in phenol formaldehyde (PF) resin synthesis, could partially be substituted by liquefied biomass. Both novolac and resol type phenolic resins have been synthesized from liquefied biomass.

### *2.1. Novolac type phenolic resins from acid-catalyzed liquefied biomass*

Most biomass liquefaction reactions were carried with an acid catalyst which can substantially lower the reaction temperature and increase the extent of liquefaction compared to that without a catalyst. Novolac is a thermoplastic type of phenolic resin synthesized with a phenol-to-formaldehyde molar ratio greater than one under acidic conditions. Therefore, acid-catalyzed liquefied biomass is favorable for novolac synthesis.

Two different types of synthetic methods for liquefied biomass-based novolac resins were investigated by many researchers. The first one was directly using liquefied wood as a novolac like resin and the other one was to further condense liquefied biomass with formaldehyde after liquefaction. This method will be discussed later in this review. Fig. 1 shows the schematic diagram of the preparation process of the liquefied wood based novolac like resin made with the first method. In brief, biomass was ground to fine particles (20–200 mesh), mixed well with phenol and an acid catalyst at designed ratios and subjected to liquefaction. After liquefaction reaction, methanol was added to dilute the thick liquid, followed by filtration to remove un-liquefied wood residue. The filtrate was first neutralized of the acid catalyst from liquefaction and then subjected to reduced-pressure evaporation at 50 and 180 °C to remove methanol and un-reacted phenol, respectively, to yield liquefied wood resin. Lin et al. [12,13] fabricated the novolac like liquefied wood resin from $H_3PO_4$ catalyzed wood liquefaction and investigated its thermal and mechanical properties. They found that the amount of reacted phenol during liquefaction increased with the increase of liquefaction temperature, time, catalyst content, and phenol to wood ratio. The flowing temperature and viscosity of the resin increased with the increasing amount of reacted phenol, which was explained as the result of the cohesiveness of the liquefied wood components becoming larger when more phenol reacted with wood. A molding compound was prepared by mixing 37.7 wt% such liquefied wood resin with 49.5 wt% wood flour as the filler, 9.4 wt% hexamine as the cross-link agent, 2.4 wt% $Ca(OH)_2$ as the catalyst, and 1.0 wt% zinc sterate as the release agent. The mechanical and physical properties of the molding products were tested and compared with commercial novolac resin. The flexural strength of the liquefied wood resin moldings was enhanced with an increasing amount of reacted phenol and became comparable to that of the commercial control when the amount of reacted phenol reached 75%. However, the water sorption test showed that liquefied wood moldings had higher water diffusion coefficients than that of the commercial novolac control, indicating that the liquefied wood resins are more hydrophilic than the petroleum based control. At the same time, liquefied

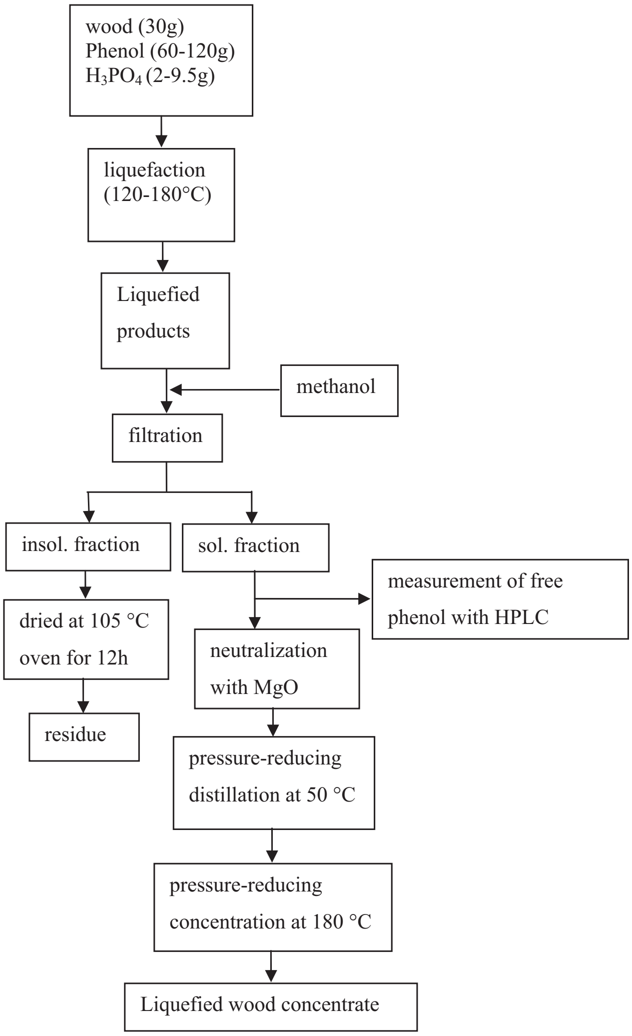



**Fig. 1.** Flowchart of liquefied wood resin preparation [12].

wood resins with higher reacted phenol were less hydrophilic than those with lower reacted phenol. Scanning electronic microscopy observations also showed that liquefied wood resin displayed better compatibility with wood filler than commercial novolac. Alma et al. [14] used the same method as in Lin's work but changed the catalyst to hydrochloric acid (HCl). They reported very similar results on the mechanical and thermal properties of the obtained novolac like resins as those from Lin's work. In general, liquefied wood resin had higher viscosity and water adsorption than the commercial novolac. One of Alam's studies [15] investigated the bio-degradability of the liquefied wood resin and the result showed that it had significantly better bio-degradability than the petroleum based novolac. One controversial point which needs to be noted is that both Lin and Alma's works used 'combined phenol' as a measurement to assess the liquefaction reactions. However, they defined the combined phenol differently [12,16]. As compared in details of these two calculation methods, it can be generally summarized that in both methods, the higher the combined phenol, the less the un-liquefied wood residue and the more completed the liquefaction reaction.

Lee and Wang [17] studied the effect of water on wood liquefaction and the properties of obtained liquefied wood resin. They report that the addition of water during liquefaction could somehow lower the melt viscosity of resulted resin, and at the same time lower the flexural strength and toughness of the moldings from liquefied wood resin. The application of liquefied wood resin in extrusion wood plastic composite (WPC) has been done by Doh et al. [18,19]. Novolac like liquefied wood resin was blended with other thermoplastic polymer such as low density polyethylene (LDPE) and high density polyethylene (HDPE) and extruded as pellets. Test specimens were then prepared from the pellets by injection. Compared to their original forms, the addition of liquefied wood resin decreased the thermal stability of all petroleum thermoplastics that were investigated in the study. The effects of liquefied wood resin exhibited opposite trends on the strength and modulus of the WPC. Both the flexural and tensile strengths of the WPC decreased while for both the modulus increased with the 10% addition of liquefied wood resin. However, no further explanation was given on the different trends of the strength and modulus. A new application of phenol liquefied wood resin was reported by Zhao et al. [20]. Phenol liquefied wood was used as a replacement for phenolic resin and mixed with wood powder to prepare wood-ceramics. They suggested that phenolic resin could possibly be substituted totally by phenolated wood, although the compressive strength of the latter was lower than that of a middle density fiberboard/PF resin wood-ceramics. Other biomass species, such as wood bark and oil palm fruit bunch, were also liquefied to make novolac like resin [21–23]. Similar results of the resin properties to those of liquefied wood resins were reported.

Most studies on biomass liquefaction have investigated the effect of liquefaction solvent to biomass ratio. The results implied that liquefaction solvent plays a double functional role during the liquefaction reactions. It reacts with the reactive sites on biomass components while it also dissolves reaction intermediates and final products, thus shifting the reaction to the liquefying direction and preventing the re-condensations of decomposed biomass components. Consequently, an excessive amount of liquefaction solvent is necessary to achieve a satisfactory liquefaction. In the case of phenol liquefaction, a quite large amount of un-reacted phenol after the reaction was reported. As shown in Fig. 1, to obtain final liquefaction products, un-reacted phenol was removed by distillation at 180 °C under reduced pressure, which was an energy consuming and impractical process. A method was proposed to overcome this problem by reacting the phenol remaining from liquefaction with formaldehyde in situ to obtain the liquefied wood phenol formaldehyde (LWPF) novolac resin. Lin et al. [24] studied the thermal and mechanical properties of the LWF resins from phosphoric acid and oxalic acid catalyzed liquefied wood. The amount of un-reacted phenol from liquefaction was used to determine the amount of formaldehyde added in resin synthesis, which was fixed at formaldehyde/phenol (F/P) molar ratio of 0.8/1. The amount of phosphoric acid added in the liquefaction stage has sufficient efficacy for the subsequent liquefied wood mixture/formaldehyde condensation reaction. The conversion of un-reacted phenol to resin was up to 94% when the content of phosphoric acid was 3.8% during the liquefaction stage. When oxalic acid was used in the liquefaction, an extra amount of oxalic acid was added during the resin condensation stage to improve the conversion of un-reacted phenol. The obtained LWPF resins from both catalysts have substantially lower flow temperatures and melt viscosities than the liquefied wood resins prepared with the first method and were close to those of commercial novolac. The mechanical properties of the molding products made from LWPF resins were also improved drastically compared to those from direct liquefied wood resin and even somewhat superior to the commercial novolac.

Alma et al. [25] investigated the effect of F/P ratio on the properties of resulted LWPF resins. They found that the average molecular weight of the LWPF resin was not affected by the F/P ratio at a small F/P ratio (less than 0.5). However, it increased rapidly with the increase of the F/P ratio when it larger than 0.5. A similar

trend was observed with the flow temperature of the LWPF resins. The flow temperature remained at about 75 °C at a F/P ratio less than 0.5. With a further increase in the F/P ratio to more than 0.5, the flow temperatures of the LWPF resins increased remarkably and were close to that of commercial novolac. It is expected that these two parameters of the LWPF resins were parallel to each other, since in general, the thermal flow properties of a polymer are closely associated with its molecular weight. The mechanical properties of the molding products did not change significantly with the changes in the F/P ratios and all the LWPF resins showed comparable mechanical properties with those of the commercial novolac resin. The electrical volume resistivity of the LWPF molding products increased slightly with the increase of the F/P ratios and was similar to that of the commercial novolac resin when the F/P ratio was 0.8, which indicated that the LWPF resin could be used for electrical appliances. One interesting point regarding the determination of the F/P ratio for the LWPF resin synthesis was addressed by Lee and Chen [26]. It would be assumed that the reactive sites on wood components, reacted phenol, and un-reacted phenol could all react with formaldehyde during the LWPF resin synthesis. However, they found that if the full liquefied wood was hypothesized as phenol and the molecular weight of phenol was used as a basis to determine the ratio with formaldehyde, some insoluble and infusible cured products were formed quickly. Therefore, the amount of un-reacted phenol from the liquefaction stage was mostly used to determine the F/P ratio in the LWPF resin synthesis. Lee and Chen also reported that the LWPF resins in their study were synthesized without external heating. The reaction between the liquefied wood and formaldehyde was an exothermic reaction, and the heat released from the reactions could increase the temperature of the system to 76 °C in a $H_2SO_4$ catalyzed system and 106 °C in a HCl catalyzed system. The yield of novolac LWPF resin powder from the $H_2SO_4$ and HCl catalyzed liquefied wood was 85.4% and 67.2%, respectively.

Pan et al. [27,28] investigated the LWPF resin prepared in a pressurized reactor and compared it with that in an atmosphere reactor. The reaction conducted under pressure resulted in less wood residue and smaller molecular weight than those from the atmospheric system at the same time and temperature, which indicated more completed liquefaction under the pressurized reaction. The cure kinetic study showed that the curing activation energy of the LWPF resins was higher than the typical novolac resin, possibly due to the less reactive of the LWPF resin than the commercial one. The water soaking and boiling tests of the composites made from LWPF resins showed that the LWPF resin from pressurized liquefaction had higher thickness swelling than those from the atmospheric liquefaction. As discussed in earlier section, LWPF resin is more hydrophilic than petroleum based commercial novolac due to the hydrophilic wood components incorporated in the resin. In addition, during the polymerization reaction of liquefied wood mixture with formaldehyde, the decomposed wood component, such as the phenolic units from lignin, was less reactive than phenol in that the C3 and/or C5 position of the benzene ring are occupied by methoxyl groups. Therefore, lower cross-linking density in LWPF resin than the commercial novolac is expected, and it could decrease with the increase of the incorporated wood components in the resin, such as in the case of the LWPF resin from pressurized liquefaction. Lee et al. [29,30] liquefied waste paper and corn bran with phenol and further reacted the liquefied mixture with formaldehyde to form LWPF resins. Improvement in resin properties was also reported when compared the LWPF resin with the direct liquefied wood resin. The application of LWPF resins has been expanded to spinning fibers [31]. Phenol liquefied wood was mixed with hexamethylenetetramine and heated to 120 °C to obtain the spinning solution. Fibers were spun from the solution and cured by soaking in a mixed solution of HCl and formaldehyde. The authors claimed that the mechanical properties of the liquefied wood fiber were better than that of the PF resin based fibers.

### *2.2. Resol type phenolic resins from acid-catalyzed liquefied biomass*

Resol type phenolic resin is thermosets and synthesized with phenol to formaldehyde molar ratio less than one under alkaline conditions. Although resol resin is more versatile regarding the molar ratio of F/P, catalysts and reaction conditions than the production of novolacs, only a few studies have been focused on resol phenolic resins from liquefied biomass, which could be due to an extra step being needed to neutralize the acidic liquefied biomass before resin synthesis. Hassan et al. [32] have studied the synthesis resols from phenol liquefied wood and applied the resin for particleboard bonding. Instead of using un-reacted phenol to determine the amount of formaldehyde, these authors applied a formaldehyde reactivity test to determine an optimum amount of formaldehyde for the resin synthesis as following: liquefied wood was mixed with NaOH, water, and excessive amount of formaldehyde, and the reaction was kept at 60 °C for 5 h. Samples were taken out of the reaction at 30 min intervals and titrated for free formaldehyde. The amount of free formaldehyde was used to calculate the equivalent of formaldehyde reacted per 100 g of liquefied wood. Neutralized liquefied wood was then reacted with equivalent formaldehyde until the desired viscosity of the resol resin was achieved. The synthesized resins showed good viscosity stabilities, expected resin solid levels, and good sprayability with a compressed air sprayer. The panels made from the resol resin had comparable modulus of rupture and modulus of elasticity with the urea–formaldehyde (UF) control resin. However, the strengths of the internal bonding of the panels were lower than the UF control, which indicated that the resin could cure adequately when it was used in the face layers but could not fully cure in the core layers. Longer hot-press time may be needed for full cure in the core layers. The panels also showed better dimensional stabilities than those made from the UF controls.

The catalyst for the resol synthesis has a great influence on the molecular structure of the resin and therefore, the later application properties of the resins. Yuan et al. [33] investigated the effect of NaOH catalyst on the properties of the resol resins made from liquefied wood bark. Larch bark was liquefied with phenol at 130 °C for 90 min. Phenol to bark ratio was 5/2 (w/w). A mixture of $H_2SO_4$ and $H_3PO_4$ was used as the catalyst at 5% of the weight of phenol. More than 90% of bark was liquefied at the above condition. Resol resins were synthesized by different methods that contained 2- or 3-step additions of NaOH. The ratio of formaldehyde to liquefied bark was fixed at 0.53 (solid basis). The amounts of NaOH added in step 1 and step 2 were fixed at 4.5% and 20.5% based on the weight of liquefied bark (solid base). An extra amount of NaOH addition in step 3 varied from 0 to 6% (0% was the addition of water). The addition of NaOH at step 1 was to neutralize the acid catalyst remained from liquefaction as well as to adjust the pH of the liquefied bark to about 9–10. The resin prepared with 2-step addition of NaOH had a higher viscosity and shorter storage life than those with an extra 3rd addition of NaOH or water. However, the storage life of all liquefied bark resols were lower than the PF control (60 days), which implied that the liquefied bark resins were more reactive than the PF control. In general, the storage life of the resin prepared with the 3rd addition of NaOH decreased as the amount of the 3rd charged NaOH increased. The longest storage life of the liquefied bark resol was 40 days and was achieved with the addition of water at step 3 (0% addition of NaOH). Wet shear strength and free formaldehyde emission were evaluated for the plywood bonded with the liquefied bark resols. The wet shear strength and wood failure decreased with the increase of the 3rd charged NaOH. The resins with 3rd NaOH charge of 0 and 2% obtained the shear

strength that exceeded the Chinese national standard for commercial plywood. The free formaldehyde emissions of liquefied bark resols were higher than the PF control, but all meet the national standards of China and Japan.

Li et al. [34] used liquefied wood to synthesize resol type phenolic resins and obtained resins with different properties than those in Yuan's study. Wood was liquefied with phenol and $H_2SO_4$ at 150 °C for 90 min using a phenol/wood/$H_2SO_4$ ratio of 0.7/1/0.05 (w/w/w). Liquefied wood was neutralized with NaOH before resin synthesis. Resol type resins were prepared with liquefied wood and formaldehyde using NaOH as a catalyst at 60 °C for 1 h and 85 °C for another hour. The total amount of phenol initially used for liquefaction was used as the basis to determine the F/P ratio. Different F/P ratios were investigated. On average, the viscosities of liquefied wood resols were higher than the commercial resol control. However, when the F/P ratio was greater than 1.8, the viscosity of the resulting resin was lower than the control due to the dilution effect by aqueous formaldehyde. The gel time of the liquefied wood resols were all longer than that of the commercial control, which according to the authors was attributed to the less activities of the liquefied wood resol. This result was quite different from those from Yuan's study [33]. Considering the complexity of liquefied wood compositions, differences in results between studies is understandable in that even small changes in synthesis conditions could change the reaction intermediate to result in different final products. Liquefied treated creosote wood was also used to synthesize both resol and novolac type phenolic resins [35]. The synthesis process and the properties of resulting phenolic resins were reviewed most recently by Effendi et al. [10].

Wang et al. [36,37] liquefied corn stalk in hot-compressed phenol–water to convert into bio-oil phenolic feedstock for the synthesis of resol type phenolic resin. This liquefaction was carried at 300–350 °C and pressurized to 2.0 MPa with nitrogen. The ratio of phenol to water was 1/4 (w/w). This kind of liquefaction should be categorized rather as a hydrothermal conversion than a thermochemical one, because water was the major reaction medium. Phenol was said to act as a capping agent to prevent the degraded lignin intermediates from forming char. The liquid fraction (i.e., bio-oil) was used to prepared resol resin. Ten grams bio-oil, 10 mL ethanol, and 0.5 g NaOH were first mixed well, and the reaction temperature was raised to 80 °C, where 12 mL of 37% formaldehyde was added drop wise. The reaction time was 2 h, and a dark, viscous resin was obtained after reduced-pressure evaporation of ethanol at 60 °C. The bio-oil resol has a greater molecular weight and higher polydispersity than the commercial PF resol. It also has shorter gel time than the control due to the higher molecular weight. The thermal stability of the bio-oil resol is satisfactory even though the residual carbon content was lower than the commercial PF control at the same temperature. This may be explained by the fact that there are many side aliphatic chains in the bio-oil resol, and these side chains are deemed to thermally decompose at much lower temperature than aromatic structures that dominate in petroleum based PF resin.

### 2.3. *Phenolic resins from alkaline-catalyzed liquefied biomass*

Some attempts have been made to liquefy biomass with phenol under alkaline conditions and the properties of both resol and novolac resins synthesized from such liquefied wood were evaluated [38–40]. Wood meal, phenol, NaOH aqueous solution (48%) were mixed and reacted in a closed pressure-proof tube at 250 °C for 1 h. Characterization of the liquefied mixture showed that liquefaction under such conditions resulted in substantially higher un-reacted phenol than strong acid catalyzed liquefaction. The percentages of un-liquefied wood residue were less than 5% under most tested conditions, indicating that most wood components have decomposed under such high temperature and alkaline conditions. However, phenol did not show good reactivity with decomposed wood components, nor undergo condensation by itself. The initial pH value of the reactants was above 9 with the existence of NaOH, and it turned to below 5 after liquefaction because of the acidic substances generated during liquefaction from decomposed wood components, mostly cellulose and hemicellulose derivatives. To synthesize resol type phenolic resin, extra amount of NaOH aqueous solution was needed to adjust the pH of liquefied wood to 9 to facilitate the addition reaction with formaldehyde. The F/P ratios were 1/1, 1.5/1, and 2/1. It is noted that the existence of un-reacted phenol was up to 12% even after the liquefied wood reacted with excessive formaldehyde. It could be due to the reactions between formaldehyde with decomposed wood units, which caused the lack of formaldehyde to react with phenol at the pre-set F/P ratio. The dry shear strength of the plywood using the above synthesized resols could meet the Japanese national standard of 1.0 MPa for plywood. However, most plywood specimens delaminated during the boil-dry-boil cyclic test for wet shear strength. Ten percent of polymeric methylene isocyanate resin was mixed with the liquefied wood based resols to improve the wet strength of the plywood. Alma et al. [41,42] used the same method to prepare resol type resin and received similar results. They also prepared novolac resins by adding formaldehyde and oxalic acid after liquefaction under the same conditions as that of the resol resins [39]. The obtained novolac resin had higher flow viscosity than the commercial novolac, and the value was substantially high with higher phenol to wood ratio during the liquefaction stage. Molding products from this novolac resin were fabricated using the same formula as in Lin's work [24]. The flexural strength of the moldings from this resin was lower than that of the commercial control. Nevertheless, the MOE of the moldings were mostly higher than the commercial control except for the resin from the lowest F/P ratio. The amount of phenol used in liquefaction was an essential parameter for the dimensional stability and degradability of the resulted resins. The molding products made from the higher phenol/wood ratio during liquefaction had lower thickness swelling, lower water adsorption, higher resistance to natural degradation, and lower weight loss in the soil decay test.

## 3. Polyurethanes from liquefied biomass

Polyurethanes (PU) are one of the most versatile materials today. Their many uses range from flexible foam in upholstered furniture to rigid foam as insulation in walls and roofs, to thermoplastic polyurethane used in footwear, to coatings and adhesives. This review will only cover the resin products. Polyurethanes are produced by reactions of one group of compounds with an isocyanate group and one group with hydroxyl groups. Biomass is naturally rich in hydroxyl groups, and liquefied biomass with polyhydric alcohols has been studied as polyols for polyurethane production. A liquefied wood polyurethane adhesive for wood laminate was prepared by Lee and Lin [43]. Polyethylene glycol with average molecular weight 400 (PEG-400) and glycerol were used as liquefaction solvents at the weight ratio of 9/1. One third of the total wood, liquefaction solvent, and $H_2SO_4$ were mixed and heated to 130 °C, followed by the addition of the other 2/3 of the wood meal. Then the reaction temperature was raised to 150 °C and kept at that temperature for 90 min. The weight ratio of liquefaction solvent/wood/$H_2SO_4$ was set at 3/1/0.09. The acid and hydroxyl values were measured to determine the isocyanate and liquefied wood polyol ratio (i.e., NCO/(OH + COOH) molar ratio). Liquefied wood polyols, organosiloxane as surfactant, and dibutyltin dilaurate as catalyst were pre-mixed well before the addition of isocyanate. Once all ingredients were mixed well, the resin was applied to

wood stripes with the amount of 200 g/m$^2$. The glued specimens were cured at room temperature under 150 kgf/cm$^2$ pressures for 24 h. Among the three different isocyanates that were investigated in their study, PMDI, Desmodur L, and Desmodur N, the PU resin prepared with Desmodur L had a suitable gel time for glue processing. Increasing the molar ratio of NCO/(OH + COOH) could increase both the dry and wet bonding strength of the liquefied wood PU resin. This might contribute to the higher cross-linking density of the cured glue-line.

Juhaida et al. [44] prepared a wood laminating adhesive from liquefied kneaf core (KC) with PEG1000/glycerol binary solvent. The weight ratio of solvent to KC was 18/1 and was higher than that of most other liquefactions. The acid catalyst, $H_2SO_4$, content was also high since it was based on the weight of the liquefaction solvent. To synthesize PU resin, liquefied KC reacted with toluene-2, 4-diisocyanate (TDI) in dioxane for 2 h at temperature of 50–60 °C. 1, 4-butanediol (BDO) was added subsequently and the temperature was raised to 70–80 °C and kept for another 3 h. The liquefied KC PU resin was then obtained after removal of dioxane by evaporation. A weight ratio of 55.0% (0.02 mol) liquefied KC polyol, 42.5% (0.19 mol) TDI, 2.5% (0.02 mol) BDO and 1% amine catalyst was considered to be able to produce reasonably good bonding. The resin was applied on the rubber wood block at a spread rate of 150 g/m$^2$, double glue line. The wood blocks were pressed together using a clamp and cured for 24 h and then conditioned at 20 ± 2 °C and 65 ± 5% relative humidity for one week prior to testing. The shear strength of liquefied KC resin was 2.9 MPa and lower than a control PU resin of 4.6 MPa. Air bubbles formed from the liberation of carbon dioxide during adhesive curing was identified as the cause of the poor bonding quality of the liquefied KC resin.

Mishra and Sinha [45] reported the preparation of a PU wood adhesive from waste paper and castor oil. Waste papers were first de-inked by washing with detergent and 1.5% NaOH solution in two steps and dried at 90 °C for 24 h. About 5 g of de-inked paper was mixed with 150 mL ethylene glycol (EG) and 0.5% acid catalyst (based on the weight of EG). The mixture was refluxed at 145–150 °C for 2.5 h. This process was described as glycolysis and the scheme is shown in Fig. 2. Un-liquefied wood residue was removed by filtration after acetone dilution. Acetone and unreacted EG were distilled at 150 °C with reduced pressure. The yield of glycoside was 93% when p-toluenesulfonic acid (PTSA) was used as the catalyst. The resulting glycoside was used to synthesize polyols with castor oil. The reaction was carried at 220–250 °C for 1 h with lithium hydroxide as the catalyst. Fig. 3 shows the reaction scheme. The hydroxyl value of obtained polyols could be adjusted by varying the ratio of glycoside and castor oil. Adhesives were prepared by mixing the polyols, TDI, and catalyst at different NCO/OH ratios. All ingredients were mixed thoroughly for 1 min and were used within 2 min of their preparation. Polyols that had higher hydroxyl value had lower viscosity. The lap shear strength of the adhesive joints was found to increase linearly with increase in hydroxyl value of the polyols, which was considered as the increase in cross-linking density of the PU adhesives. Prepared adhesives with the best performance had even higher shear strength than two of the commercial PU controls. Five days were required for the resins to completely cure and reach their ultimate strength. The PU adhesives from liquefied wood had good resistance to water and moderate resistance to acid treatment, but were not resistant to alkaline treatment. Overall results from the thermogravimetric (TG) analysis showed that the resins had better high temperature stability than the requirement of the application for wood adhesives.

PU films were prepared from the polymerization of PEG/glycerol liquefied wood and PMDI [46–48]. Wood meal was liquefied with PEG 400/glycerol at ratios from 1/2 to 1/9 (w/w) with 3% $H_2SO_4$ as the catalyst. Liquefaction temperature and time was 150 °C and 75 min. Liquefied wood was diluted with dioxane/water to remove wood residues and was neutralized before the evaporation to obtain concentrated liquefied wood with 0.6–0.8% water content. Liquefied wood was mixed with PMDI at NCO/OH ratio from 0.6 to 1.4 without catalyst and surfactant. The mixture was agitated for 10 min before being poured into Petri dishes to make films. The cast films were gradually dried below 7 °C for 3 days, and then conditioned at 20 °C, 65% relative humidity for 11 days. Finally the films were heat-treated at 100 °C for 8 h. Properties of resulted PU films were evaluated. The cross-linking density in cured films increased with the increase of NCO/OH ratios. The glass transition temperature (Tg) of the films increased as the result of the increased cross-linking density in the films. The increase in the wood content (i.e., the decrease in solvent/wood ratios during liquefaction) also caused the increase of cross-linking density in the films, which indicated that the wood components in the film acted as cross-linking agents rather than as a chain extender. The tensile test of the film showed that both the Young's modulus and tensile strength increased while the maximum elongation decreased as the wood content in the films increased. Since the weight proportion of PMDI

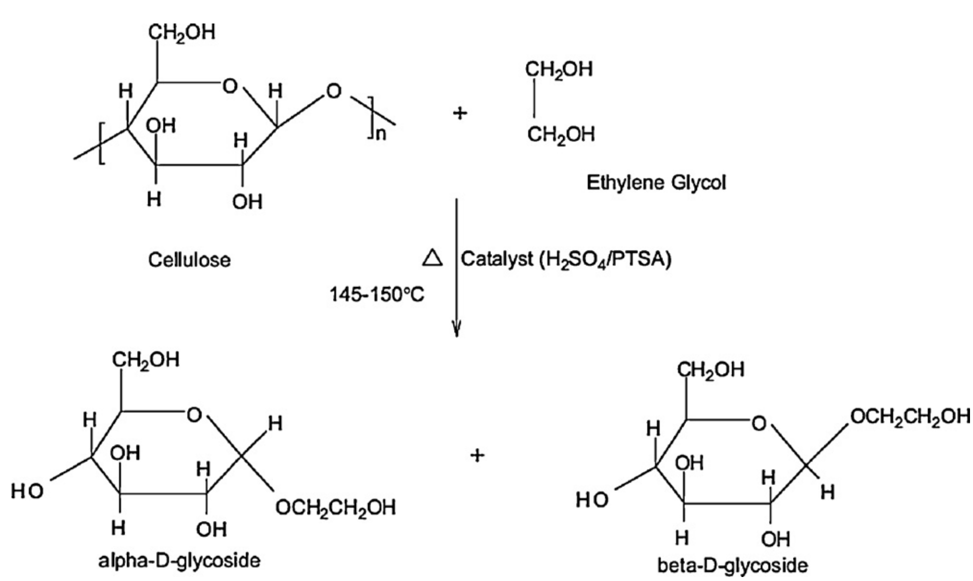



**Fig. 2.** Glycolysis of de-linked waste paper [45].

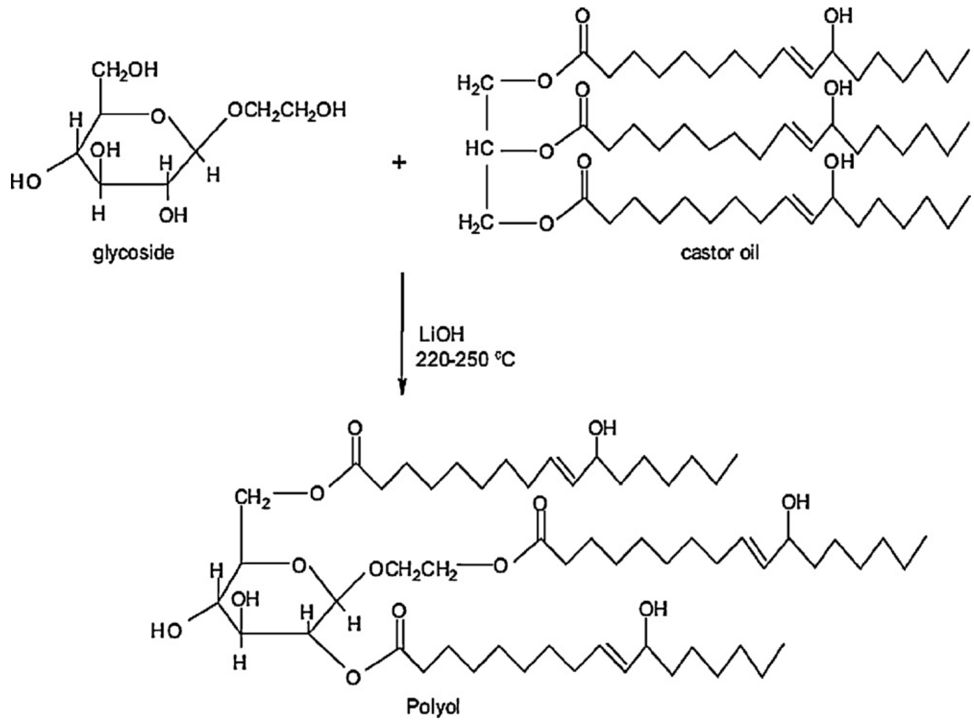



**Fig. 3.** Synthesis scheme of polyol from waste paper glycoside and castor oil [45].

to liquefied wood decreased from 47.6% to 43.8% with the wood content increased from 5.0% to 10.8%, the rigid mechanical properties with increased wood content should not due to the extension of cross-linking between liquefied wood and PMDI, though the increase of NCO/OH ratio would enhance the mechanical properties of the films. This might suggest that the wood fragments incorporated in the PU films possibly increased its stiffness. The liquefied wood PU film made from a NCO/OH ratio higher than 1.0 or wood content higher than 10.6% started degradation at about 262 °C, which was 9 °C higher than that of the commercial control.

A different liquefaction reagent, dibasic ester (DBE), for PU resin preparation was used by Wei et al. [49–51]. Wood meal was first treated with benzyl chloride. Benzylated wood (BW) was then liquefied by DBE and HCl as a catalyst at 75–80 °C for 3 h. After removal of un-liquefied BW, liquefied mixture was used to synthesize PU resins as follows: liquefied BW was mixed with a small amount of PEG as a plastisizer and stirred for 30 min at 50 °C. Then a defined amount of pre-mixed diisocyanate and butylacetate was added gradually followed by a quick addition of dibutyltin as a catalyst. The reaction was kept at 50 °C for 30 min after the additions of all ingredients, and raised to 75–80 °C and continued to react at the same temperature for 3 h. PEG with different molecular weight and 3 different diisocyanates, hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI), and TDI were investigated for the synthesis of the PU resins. The TG and differential thermal (DTA) analysis indicated that the liquefied wood based PU resins had higher thermal stability (280 °C) than the petroleum based PU (<250 °C). TDI exhibited the best performance to prepare PU for painting applications, while HDI is not suitable for this system. The molecular weight of PEG as the plastisizer for the PU film had no profound effect on the thermal properties of the films.

## 4. Epoxy resins from liquefied biomass

Epoxy resin is a thermosetting polymer resulting from reaction of epoxide with polyamine (curing agent). The epoxy resin has a wide range of applications as surface coating materials, moldings, composite, and engineering adhesives, by virtue of its toughness, flexibility, mechanical strength, and chemical resistance. The most widely used epoxy resin is made by condensation of epichlorohydrin with bisphenol A or diphenylol propane. Other hydroxyl containing compounds, including resorcinol, glycols, and glycerol, can replace bisphenol A. Kobayashi et al. [52–54] studied the application of liquefied wood to epoxy resins. Wood was liquefied with PEG400/glycerol (4/1, w/w) and $H_2SO_4$ (3% based on PEG/glycerol) at 170 °C for 3 h. To make epoxy resin films, liquefied wood was mixed with an epoxide and left for 24 h at room temperature. Triethylene tetramine (TETA) was then added as a curing agent. The mixture was casted onto a Teflon sheet and the film was first cured at room temperature for one day, then followed by heating at 90–150 °C for 1–9 h. Cured liquefied wood epoxy resins had lower Tg than the petroleum based epoxy resin. They were in a transient region between a glassy state and a rubbery state at room temperature. This could be resulted from the low molecular weight components in liquefied wood, and they would act as a plastisizer in the cured epoxy resins. Liquefied wood epoxy resins also had higher curing temperature than the commercial epoxy resin, and the temperature shifted to a higher region when the liquefied wood content increased in the resin. The dry shear strength of liquefied wood epoxy resins was comparable to the commercial control but the wood failure was much lower. When subject to cyclic boiling test, it showed inferior properties regarding both the shear strength and wood failure than the petroleum based control. Asamo et al. [55] pretreated wood with ozone before liquefaction to synthesize liquefied wood epoxy resin with high wood content. Wood meal was dispersed in a dioxane and methanol mixture at 0 °C while the oxygen containing 3% ozone was introduced into the wood meal with stirring. The treating time was 16.3 min per gram of wood, and the amount of ozone reacted with wood was calculated as 0.23 g per gram wood. After the treatment, wood was liquefied with PEG/glycerol at relatively low liquid/wood ratios (1/1, 1/1.5, and 1/2, w/w) at 150 °C. Synthesis of liquefied wood based epoxy resin was followed the same method as in Kobayashi's work. The wood content in the resulting epoxy resin could reach 53%. The

tensile strength of this high wood content epoxy resins was said to be at the same level as commercial melamine–formaldehyde resins or phenolic resins. A similar method to Kobayashi's work was also used to synthesize epoxy resin from ethylene carbonate liquefied bagasse [56]. The resulting epoxy resin showed different properties than that from PEG/glycerol liquefied wood. The Tg of the cured epoxy resin with 25% liquefied bagasse was 230 °C and was much higher than the pure petroleum based epoxy resin (111 °C) cured under the same condition. The degradation temperature of liquefied bagasse based epoxy resin was also slightly higher than the pure epoxy resin. The better thermal properties of the ethylene carbonate liquefied bagasse epoxy resin was ascribed to the rigid aromatic structure and highly branched lignin derivatives in liquefied bagasse.

Resorcinol liquefied wood was used to substitute bisphenol A in epoxy resin synthesis [57,58]. The liquefaction was carried at resorcinol to wood ratio 1/1 or 2/1 at 250 °C without catalysts or 150 °C with $H_2SO_4$ at a catalyst. To synthesize epoxy resin, excessive epichlorohydrin and liquefied wood were mixed and reacted at 100 °C. NaOH (50%) solution at twice the molar ratio to the phenolic OH groups was added drop-wise while stirring. The reaction was kept at the same temperature for another 2.5 h to achieve the addition reaction of epichlorohydrin and the ring formation of epoxy groups. The reaction byproducts were filtrated after diluting the reaction mixture with acetone. Then acetone and un-reacted epichlorohydrin were evaporated at 80 °C under reduced pressure. The resulting epoxy resin was cured with 4,4′-diamino diphenyl methane (DDM) as the cure agent at 130 °C for 4 h, then at 150 °C for 2 h. The cured wood based epoxy resins showed high stiffness at room temperature and a clear rubbery plateau after Tg, which was lower and in a broader region than those of the bisphenol A based epoxy resin. A broad Tg region suggested a diversity of cross-linking structures in cured resin. The flexural strength and modulus of liquefied wood based epoxy resins were more than equivalent to that of the petroleum based epoxy resin. This epoxy resin was used as matrix resins to fabricate nature fiber reinforced composite with flax fibers and ramie fibers. Observations of the fracture surface of the composite implied that the wood based epoxy resin had better compatibility with the reinforced fiber than the petroleum based epoxy resin. The stiffness and strength of the wood based epoxy resin composite were comparable to those made from commercial epoxy.

Wu and Lee [59] evaluated the epoxy resins synthesized from phenol liquefied wood and PEG/glycerol liquefied bamboo. The synthesis started with the reaction of epichlorohydrin and bisphenol A (molar ratio 5/1) at 110 °C for 2 h under stirring and dripping of aqueous NaOH. Then liquefied bamboo and additional epichlorohydrin were added and reacted at the same temperature with dripping of the rest of NaOH for another 2 h. The total amount of NaOH added was 1 mol. The epoxy resin was obtained after filtration of byproduct NaCl and removal of un-reacted epichlorohydrin and water by reduced pressure distillation. Phenol liquefied bamboo was more suitable than PEG/glycerol liquefied bamboo in epoxy resin synthesis. The resulting epoxy resin had similar curing behavior to the petroleum based epoxy resin. The thermal degradation temperature of liquefied bamboo epoxy resin was lower than that of the petroleum control. However, the epoxy resin from phenol liquefied bamboo had less weight loss (i.e., higher char content) at temperature higher than 700 °C than the petroleum based epoxy resin.

## 5. Other resin products from liquefied biomass

The most studied applications of liquefied biomass to polymers are phenolic resin and followed by polyurethane and epoxy resins due to those specific functional groups, such as phenolic and hydroxyl, existing in biomass. A few studies have been done on application areas other than those three major polymers. For instance, Kunaver et al. [60] used glycerol/diethylene glycol (4/1, w/w) as liquefaction solvent to obtain liquefied wood with high hydroxyl group content. A small amount of diethylene glycol in the binary solvent was to reduce the viscosity of the final resin products so that they can meet the application requirement. Liquefaction was conducted at 180 °C for 3 h using p-toluenesulfonic acid as the catalyst (3% based on the weight of liquefaction solvent). The resulting liquefied wood was blended with commercial urea–formaldehyde (UF), melamine–formaldehyde (MF), or urea–melamine–formaldehyde (MUF) resins and used for making particleboard. Blending of liquefied wood to the UF, MF, or MUF increased the gel time of the pure resins, and they increased with the increasing loading amount of liquefied wood. Addition of liquefied wood to the MF and MUF resins could reach to 50%, and the particleboard made with these resins could attain satisfactory properties required by the European particleboard standard. The formaldehyde emissions of the panels made from liquefied wood blending resins were all lower than those from pure resins without liquefied wood. The author suggested that the lignin fragments in liquefied wood could be served as a formaldehyde scavenger due to their aromatic structures. Another type of liquefied wood UF resin for particleboard was prepared by Antonoivc et al. [61]. Glycerol liquefied wood with $H_2SO_4$ as the catalyst was used directly as a substitute to phenol to synthesize novolac resin at formaldehyde/liquefied wood ratio 0.75/1. The resulting resin was adjusted to a pH value of 7–8 by NaOH aqueous solution after synthesis. Original and alkalized liquefied wood were both used to blend with a commercial UF resin at 10–20% for particleboard making. The tensile and bending strength of the panels using the blending resin in core layers were slightly lower than the standard value, but the thickness swelling was substantially higher than the standard. Particleboard made from UF replacement with 15% liquefied wood resin had exceptionally physical and mechanical properties, except for the high free formaldehyde emission, which indicated that the formaldehyde added for the resin synthesis did not completely react with liquefied wood as expected.

Liquefied wood was also blended with PMDI and used as water based polyisocyanate adhesives (API) [62]. PEG400/glycerol (7/3, w/w) and $H_2SO_4$ used as the liquefaction solvent and catalyst, respectively. Liquefaction was carried with the following conditions: solvent/wood ratio 3/1, temperature 150 °C, time 1.5–5 h. An equivalent amount of 40% NaOH was added to neutralize the acid catalyst after liquefaction. Liquefied wood isocyanate (LWI) resins were prepared by blending 100 parts of liquefied wood with 158 parts of PMDI. The total solid content of the LWI was more than 90% and higher than that of a commercial API at about 66%. The LWI resin was applied to plywood adhesives. Three layer plywood panels were made to evaluate the properties of the LWI resin. LWI resin was spread with 166 $g/m^2$ on both sides of the core veneer. Both the dry and wet shear strengths of the panels were lower than the commercial API resin and decreased with longer liquefaction time. Since the LWI had relatively low viscosity, the lower strength could be attributed to the over penetration of the LWI resin through the wood surface. The panels made from LWI with 1.5 h liquefaction could meet the criteria of the Japanese national standard for plywood.

Polyesters from liquefied biomass were prepared via both cross-linking and ring-opening polymerization. Corn stover was liquefied with ethylene glycol/ethylene carbonate (9/1, w/w) with $H_2SO_4$ (2% based on the liquid weight) at 160 °C for 2 h [63]. The solvent to stover ratio was 4/1 (w/w). Obtained biomass polyols had a hydroxyl value around 200 mg KOH/g and a viscosity of $2 \times 10^5$ MPa s. Polyester sheets were formed by cross-linking the

biomass polyols with various dicarboxylic acids or anhydrides. Curing temperature and time of the polyester sheets varied from 140 to 180 °C and 1–5 h depending on the formulation and the thickness of the sheet. Cyclic anhydrides were found to be a better cross-linking agent than diacid since the amount of water produced by anhydrides was only half of that by diacids. Liquefied stover polyesters were quite stable in cold organic solvents and cold water, but were much soluble in hot water, hot acid, and hot alkaline solution. The mechanical properties of the polyester were not very strong, but the strength is acceptable for some applications, such as garden mulch film. This biomass based polyester had satisfied biodegradability that the weight lost could reach to 82% in 10-month. A similar method was adapted by Kunaver et al. to synthesize polyester from liquefied wood [64]. Compared to commercial polyester, a rise of average molar mass and a reduction of the hydroxyl group content of the liquefied wood derived polyester were reported. A ring-opening polymerization of cyclic ester onto liquefied biomass to make biodegradable polyesters was evaluated by Lee and Ohkita [65]. Wood was liquefied by PEG/glycerol (4/1, w/w) at 180 °C for 3 h with $H_2SO_4$ as the catalyst. Polyesters were prepared by react cyclic esters with dehydrated liquefied wood at 140 °C for 5–120 min. The obtained polyesters had high viscosities, which increased linearly with the increase of the cyclic ester (e.g., caprolactone) to liquefied wood ratio during the ring-opening polymerization. This may be attributed to the increase of the molecular weight and the crystallinity of the poly-caprolactone.

## 6. Conclusions

Biomass liquefaction with organic solvents is a unique thermochemical conversion process for biomass utilizations. It combines the useful functional groups from both biomass and the organic solvents, thus obtaining a large variety of polymers, especially resin products. Phenolic is the most studied resin type from liquefied biomass in an attempt to utilize the phenolic units in biomass lignin as phenol substitute in phenolic resin synthesis. Further condensation reaction of liquefied biomass with formaldehyde in situ to synthesize novolac or resol phenolic resins under acidic or alkaline conditions was proven to be an efficient route to convert the unreacted phenol from liquefaction to resins and improve the physical mechanical properties of resulted resins when compared to liquefied wood resin without condensation reaction with formaldehyde. Synthesis of novolac phenolic resin from phenol liquefied biomass could be more convenient than resol type in that most liquefactions were carried out under acidic conditions to promote the liquefaction. Liquefied biomass can be used directly in novolac synthesis, whereas it needs to be neutralized to synthesize resols. Except for phenolic resins, most other polymers from liquefied biomass were synthesized based on the utilization of hydroxyl groups in liquefied biomass. Polyhydric alcohols liquefied biomass was used as polyols to synthesize polyurethanes, epoxy, and polyesters. The hydroxyl values of the biomass polyols were within the appropriate range for these applications. To achieve comparable mechanical strength of the resulting resin products, common liquefaction solvent to biomass ratio was 3/1, which indicates a biomass substitution around 25% to petroleum raw materials. A few cases could reach 50% substitution with biomass pretreatment before liquefaction.

As the author preparing this review, it can be seen that results and illustrations varied among research groups regarding similar studies. It is understandable when one consider that the biomass is such a versatile raw materials including hundreds of thousands of species. Their chemical compositions are mostly in common but still varying between species. Despite the differences in resin type, physical and mechanical properties, resin products from liquefied biomass share some general drawbacks: (1) the viscosities of liquefied biomass based resins were normally higher than their petroleum counterparts. High viscosity some time may be problematic for the application processing, especially for those using a spray method; (2) liquefied biomass based resins showed hydrophilic characters, which could be both advantageous and disadvantageous. The resins from liquefied biomass displayed good compatibilities with natural fiber in natural fiber reinforced composite fabrication. On the other hand, the composite or panels using biomass based resins had higher water adsorption and less dimensional stabilities than the petroleum base resins; (3) the mechanical strength of liquefied biomass based resins were normally lower than the petroleum based resin, in particular, in wet bonding strength. It could be due to the lower reactivity of lignocellulosic derivatives incorporated in the resin, and thus the resins had lower crosslink density compared to the petroleum based resins. Nevertheless, alleviation the production of chemicals mainly from fossil resources and turning the direction to the low cost, environmentally friendly, renewable biomass resource have been driven and are still driving the research to overcome the problems in current technologies and to make marketable products from renewable natural resources.

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